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(9) QUARTERLY REPORT NO. 4, 1 Apr - 30 Jun 64,

[redacted]

[redacted]

~~U. S. ARMY NATICK LABORATORIES~~

~~Report Period: 1 April 1964 - 30 June 1964~~

(6) SYNTHESIS AND POLYMERIZATION OF
FLUORINATED SULFUR MODIFIED
NITROSO RUBBER,

(10) BY

Eugene C. Stump and Calvin D. Padgett.

~~21 July 1964~~

(5) PENINSULAR CHEMRESEARCH, INC.,
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152

FOREWORD

This report was prepared by Peninsular ChemResearch, Inc. under Contract No. DA 19-129-(AMC)-157(N) (OI 9116) for the U. S. Army Natick Laboratories with Mr. Frank Babers as Project Officer. This is the fourth Quarterly Report under this contract and covers the period 1 April 1964 through 30 June 1964.

Personnel engaged in this research are Eugene Stump, Project Supervisor, (40%) and Calvin Padgett, Research Chemist, (100%). Analytical work was performed under the supervision of Van May. Drs. Paul Tarrant and George Butler are acting consultants.

It is estimated that 60% of the work is completed and that 70% of the estimated costs have been incurred to date. To the contractor's best knowledge the funds remaining unexpended are sufficient to complete the work called for in the contract.

ABSTRACT

Efforts to synthesize $SF_5CF(NO)CF_2Cl$ and to polymerize C_2H_5SNO are described. Several fluoroaromatic monomers and precursors have been prepared including 1, 4-dibromotetrafluorobenzene, tetrafluoroterephthalic acid, monosilver tetrafluoroterephthalate, tetrafluoroterephthalyl mononitrite and 1, 4-diaminotetrafluorobenzene. Continued efforts to prepare SF_5COOH and to synthesize SF_5CF_2COOH are described. Low temperature polymerization of thiocarbonyl fluoride with CF_3NO, $CF_2=CF_2$, and $CF_3NO/CF_2=CF_2$ using a triethylborane/oxygen catalyst has been examined. Trifluoronitrosomethane and tetrafluoroethylene were polymerized with a coordination catalyst. The reactivity of $CF_3SCF(NO)CF_2Cl$ is apparently low compared with CF_3NO since little, if any, of this compound polymerized in the system $CF_3NO/CF_2=CF_2/CF_3SCF(NO)CF_2Cl$. An attempt to prepare C_2H_5SNO and polymerize it with $CF_2=CF_2$ in situ was not successful.

TABLE OF CONTENTS

FIGURES

I. INTRODUCTION

The research described in this report is part of a continuing program sponsored by the U. S. Army Natick Laboratories and concerned with the development of so-called "nitroso rubber", a 1:1 copolymer of trifluoronitrosomethane and tetrafluoroethylene. A list of references describing prior research was given in the First Quarterly Report.

The primary objective of this contract is to enhance the desirable properties, in particular the low-temperature flexibility, of nitroso rubber by the incorporation of sulfur atoms in a modified polymer structure. Secondary objectives include the synthesis of desirable monomers, including monomers not containing sulfur, and their polymerization in the nitroso rubber system.

This report describes the synthesis of certain monomers and attempts to incorporate them into the nitroso polymer, either as comonomers or as termonomers.

II. DISCUSSION

A. Synthesis of Sulfur-Containing Nitroso Compounds

Since efforts to prepare perfluoroalkyl thionitrites such as CF_3SNO have been unsuccessful[1] an attempt to prepare a hydrocarbon analog was carried out. Ethyl thionitrite was chosen since a description of its preparation was available[2]. This synthesis consists of reaction of ethyl mercaptan and nitrosyl chloride at low temperatures. However,

$$C_2H_5SH + ClNO \rightarrow C_2H_5SNO + HCl$$

although the deep red color characteristic of thionitrites was obtained during the reaction, the desired product could not be isolated at room temperature, probably due to decomposition to give diethyl disulfide.

$$2C_2H_5SNO \rightarrow C_2H_5SSC_2H_5 + 2NO$$

Attempts to prepare this compound and polymerize it at low temperatures without isolation are described in another part of this report.

The reaction of trifluorovinylsulfur pentafluoride with nitrosyl chloride has been repeated using shorter periods of irradiation. After two hours in sunlight the vapor turned from red to a pale green. Six hours additional radiation produced no observable change. The desired adduct, $SF_5CF(NO)CF_2Cl$, was not detected in the reaction mixture.

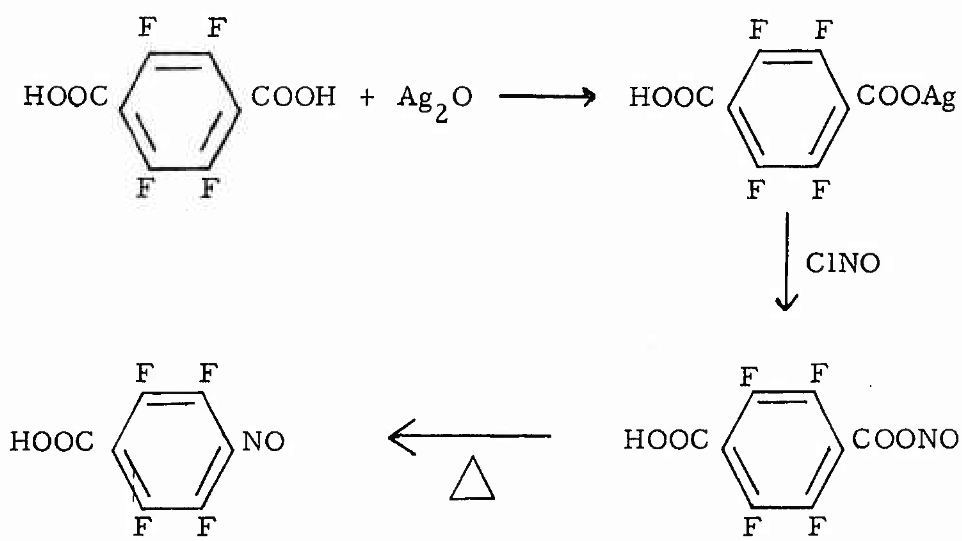
(1) Quarterly Progress Reports Nos. 1, 2 and 3 under this contract.

(2) H. Lecher and W. Siefken, Ber, 59, 1314 (1926)

B. Synthesis of Perfluoroaromatic Compounds

Pentafluoronitrosobenzene has been shown to copolymerize readily with fluoroolefins[3] and to terpolymerize with trifluoronitrosomethane and tetrafluoroethylene[3, 4]. Consequently, the use of a fluoroaromatic nitroso compound containing a second functional group might provide a crosslinking site in the polymer chain. Since workers at 3M have shown that a pendent carboxy group can give crosslinking resulting in a vulcanizate with superior properties[5], a compound such as p-nitrosotetrafluorobenzoic acid should be an interesting termonomer. Attempts to prepare this compound by the oxidation of p-aminotetrafluorobenzoic acid[6] have as yet been unsuccessful. A synthesis using lithiation of 2, 3, 5, 6-tetrafluoronitrosobenzene followed by carbonation is also being examined[6].

We are investigating the preparation of this compound by the following route.



(3) Quarterly Progress Report No. 1 under this contract, 21 October 1963.

(4) Quarterly Progress Report No. 2 under this contract, 21 January 1964.

(5) H. A. Brown, N. Knoll and D. E. Rice, "Arctic Rubber", Final Summary Research Report on Contract DA-19-129-QM-16B4, for the period 24 August 1960 - 23 December 1962.

(6) Thiokol Chemical Corp., "Nitroso Rubber Research, Development and Production", Quarterly Report No. 2 on Contract DA-19-129-AMC-69(x) for the period 1 December 1963 - 29 February 1964.

Synthesis of the monosilver salt gave a compound containing a slight excess of the theoretical amount of silver, indicating the presence of minor amounts of the disilver salt. This compound has been reacted with nitrosyl chloride to give a reaction product from which a yellow crystalline product has been sublimed. An infrared spectrum (Fig. 7) of this compound shows carbonyl, nitrite and typical fluoroaromatic absorption peaks.

In synthesizing the tetrafluoroterephthalic acid intermediate the following route was used.

$$C_6F_6 + NH_2NH_2 \rightarrow C_6F_5NHNH_2{}^{7}$$

$$C_6F_5NHNH_2 + NaOH \rightarrow p\text{-}C_6F_4H_2{}^{7}$$

$$p\text{-}C_6F_4H_2 + BuLi \rightarrow p\text{-}C_6F_4Li_2 \xrightarrow[HCl]{CO_2} p\text{-}C_6F_4(COOH)_2{}^{8}$$

An 81% conversion was obtained in the final step.

The synthesis of 1, 4-diaminotetrafluorobenzene has been completed, giving only a small amount of impure (by infrared and m. p.) material. This preparation will not be repeated due to the tedious procedure and the low yields obtained.

1, 4-Dibromotetrafluorobenzene was also required as an intermediate and was prepared by a reported procedure[9] involving the bromination of 1, 2, 4, 5-tetrafluorobenzene in 65% fuming sulfuric acid. It was found to be necessary to use fresh concentrated acid since an initial reaction using 35% fuming H_2SO_4 from stock gave only partial bromination. The attempted preparation of this compound by reaction of bromine with 1, 4-dilithiotetrafluorobenzene gave an intractable, viscous, black liquid. This synthesis

(7) D.G. Holland, G.J. Moore and C. Tamborski, Technical Documentary Report No. RTD-TDR-63-4157, January, 1964.

(8) C. Tamborski, private communication, article in press.

(9) M. Hellman and A. Bilbo, J. Am. Chem. Soc., 75, 4590 (1953)

was not investigated further although it is felt that suitable conditions could be found under which the reaction would proceed satisfactorily.

An attempt to prepare C_6F_5NO by the reaction of C_6F_5Li with nitrosyl chloride gave a solid compound containing no nitrogen. Its infrared spectrum is shown in Fig. 3.

C. Synthesis of Intermediates and other Monomers.

The attempted preparation of carboxysulfur pentafluoride, SF_5COOH, by the oxidation of $SF_5CH=CH_2$ has been described in a previous report[10]. During this quarter this oxidation was examined under different conditions (acetone/$KMnO_4$) but again no new S-F compounds were detected. One additional attempt to prepare this compound by the reaction of sulfur chloride pentafluoride and butyl lithium or magnesium followed by carbonation will be carried out.

The synthesis of SF_5CF_2NO via the unreported intermediate SF_5CF_2COOH has also been investigated. Since the reaction of SF_5Cl with $CH_2=C=O$ has been reported to give SF_5CH_2COCl[11], it may be possible to prepare the acid by the following series of reactions.

$$SF_5Cl + CF_2=C=O \rightarrow SF_5CF_2COCl$$

$$SF_5CF_2COCl + H_2O \rightarrow SF_5CF_2COOH$$

Difluoroketene has been reported[12] and its synthesis initiated using the reactions shown.

$$CF_2ClCOOH + PBr_5 \rightarrow CF_2ClCOBr$$

$$CF_2ClCOBr + Zn \rightarrow CF_2=C=O$$

(10) Quarterly Progress Report No. 3 under this contract.

(11) D. Coffman and C. Tullock, U.S. Patent 3,102,903, 3 September 1963

(12) Yarovenko, Zhur. Obshchei Khim, 27, 2796 (1957); C.A., 52, 8042(1958)

Since the dehalogenation step was reportedly run in ethyl ether which gave an azetrope with the product, we attempted the dehalogenation in tetrahydrofuran. No volatile products were obtained, however, and the reaction will be repeated in ethyl ether.

During this period another sample of $F_2C=S$ was prepared by the pyrolysis of $(CF_2S)_2$ as previously described[3].

An attempt to react nitrosyl chloride with $CF_3OCF=CF_2$, similar to the reaction of $CF_3SCF=CF_2$, did not give the desired adduct.

D. Polymerizations

Copolymerization of thiocarbonyl fluoride with olefins at low temperatures has recently been reported by workers at du Pont[13]. The polymerizations are initiated by free radicals generated by a tralkylborane/oxygen mixture. Since previous attempts to copolymerize or terpolymerize thiocarbonyl fluoride in systems such as $F_2C=S/CF_3NO$ and $F_2C=S/CF_3NO/CF_2=CF_2$ have not been successful, we have repeated these attempts using triethylborane/oxygen as an initiator. Although analysis of the polymers is not complete, it appears that the major reaction was homopolymerization of thiocarbonyl fluoride.

Polymerization of $CF_3NO/CF_2=CF_2$ has been carried out in solution using a coordination catalyst consisting of $AlBr_3$, VCl_4 and $(C_6F_5)_4Sn$. Although a viscous liquid was formed, this catalyst system apparently has no advantage over the usual procedure.

An initial attempt to incorporate the new sulfur-containing nitroso compound, $CF_3SCF(NO)CF_2Cl$, into the nitroso polymer system by terpolymerization with CF_3NO and $CF_2=CF$ gave a viscous liquid. The

(13) C. and E. News, p. 46, 16 December 1963

infrared spectrum of this compound was very similar to that of $CF_3NO/CF_2{=}CF_2$ copolymer. However, NMR analysis will be carried out to determine the possible presence of the CF_3S group.

Since ethyl thionitrites could not be isolated at room ten ·erature an attempt was made to polymerize the compound with tetrafluoroethylene in situ at -30°. No polymeric material was obtained, however.

III. EXPERIMENTAL

A. Synthesis of Sulfur-Containing Nitroso Compounds

1. Attempted Synthesis of C_2H_5SNO

A 250-ml. flask fitted with a gas inlet, thermometer, and low-temperature reflux condenser was charged with C_2H_5SH (28.9g., 0.45 moles) and cooled to -40°. The ClNO (29.5g., 0.45 moles) was added via the gas inlet tube which opened beneath the surface of the mercaptan. The solution first turned a bright pink and as more ClNO was added a deep cherry red. At this point fumes (acid to litmus) were passing through the condenser (cooled to ~-35°). The ClNO was added at a rate which kept the solution temperature at ~-15°). After about half of the ClNO was added the solution color began to lighten, and a solid was deposited. The solution shortly lost all of its dark red color.

2. Attempted Synthesis of $SF_5CF(NO)CF_2Cl$

A 1-l Vycor flask was charged with $SF_5CF{=}CF_2$ (2.3g., 11 mmoles) and ClNO (o.72g., 11 mmoles) and placed in sunlight for 2 hours. At this time the originally red overgas had turned to a pale green. The flask was left in sunlight ~6 additional hours with no noticeable change. The production mixture was separated by GLC and shown by infrared spectra to consist of SiF_4, SOF_2, SO_2F_2, SOF_4, N_2O, ClNO, $SF_5CF{=}CF_2$, and CF_3Cl.

B. Synthesis of Perfluoroaromatic Compounds

1. Pentafluorophenylhydrazine

Two separate reactions gave a total yield of 542g. of $C_6F_5NHNH_2$.

The following is a description of one reaction. Hexafluorobenzene (250g., 1.34 moles) and hydrazine hydrate (141g., 2.82 moles) were refluxed overnight with stirring in 600ml of tetrahydrofuran. About 500 ml of solvent was stripped off, and the remaining hot solution was poured into 3 liters of H_2O. A pale yellow solid formed. This material was washed several times by stirring with water and decanting; finally it was filtered, washed with water, and dried in a vacuum desiccator to yield 217g. of pentafluorophenylhydrazine as a white powder (82% conversion).

2. 1, 2, 4, 5-Tetrafluorobenzene

Three reactions were run. The following is a description of one of them.

A 5-l flask was fitted with a stirrer, reflux condenser, and tubing for addition of solids. The flask was filled with 3200 ml of 3N NaOH and the solution heated to reflux. Pentafluorophenylhydrazine (217g., 1.1 moles) was added in small amounts over a one hour period. After the last addition the solution was refluxed an additional 21/2 hours. The mixture was distilled and a two phase product was obtained. The organic layer was separated and dried over $MgSO_4$. The water layer was extracted several times with xylene and these extracts were combined with the organic distillate over $MgSO_4$. After drying, the $MgSO_4$ was filtered off and the filtrate was distilled on a spinning band column. Fractions were taken as follows:

B. P. °C	n_D^{20}	Wt. g.
90-92	1.4088	55.4
92-93	1.4098	29.1
93-98	1.4149	16.7

Infrared spectra were the same for all fractions.

3. 1, 4-Dibromotetrafluorobenzene

a. Reaction of 1, 4-Dilithiotetrafluorobenzene with Bromine

Two reactions were run. The first ended in a detonation before Br_2 was added to the dilithio compound. The following is a description of the second reaction. Butyl lithium (12. 8g., 0. 2 mole) dissolved in hexane (125ml) was placed in a flask fitted with a stirrer and addition funnel and cooled to -78°. From the addition funnel p-$C_6F_4H_2$ (15g., 0. 1 mole) dissolved in tetrahydrofuran (20ml) was added over a period of 20 minutes and then stirred an additional 40 minutes. This was followed by the addition of Br_2 (32g., 0. 2 mole) dissolved in ethyl ether (100ml). The mixture was then allowed to warm to room temperature. The reaction mixture was washed with H_2O to remove any LiCl; it was then evaporated to dryness. The product was a viscous, black liquid which was not identified.

b. Reaction of 1, 2, 4, 5-Tetrafluorobenzene with Bromine

Two reactions were run. The following is a description of one of them. A 500-ml., 3-neck flask was fitted with a stirrer, reflux condenser, and addition funnel and charged with 65% fuming H_2SO_4 (65. 5 ml), Br_2 (60. 2ml), and $AlBr_3$ (2. 2g.). The addition funnel was filled with p-$C_6F_4H_2$ (43. 0g., 0. 29 moles) which was slowly added to the solution in the flask. After the addition of $C_6F_4H_2$ was completed the solution was heated at 50-60° for 4 hours. The mixture was then poured over 4 liters of cracked ice. After the ice melted the pale yellow ppt which had formed was filtered off and washed several times with water followed by washing with Na_2CO_3 solution. The filter cake was then dissolved in methanol and precipitated by pouring into H_2O. The product (50g.) was filtered and dried. M. pt. 73-75°.

4. Pentafluoronitrosobenzene

A 250-ml flask was fitted with an addition funnel, stirrer, reflux condenser, and gas outlet vented to a trap in liquid oxygen. A solution of C_4H_9Li (6.4g., 0.1 mole) in hexane (63 ml) was placed in the flask and cooled to -78°. A solution of C_6F_5H (16.8g., 0.1 mole) in ethyl ether (40 ml) was added from the addition funnel over a 20 minute period. The mixture was stirred an additional hour. This was followed by the addition of ClNO (6.5 g., 0.1 mole) which produced a yellow solution over a brown ppt. This mixture, still cooled to -78°, was stirred overnight. There was no noticeable change when the mixture warmed to room temperature. The solid product was filtered off and washed with water to remove LiCl. An infrared spectrum showed absorption which may be due to a fluoroaromatic group. The filtrate was evaporated to dryness; the residue was washed with CH_3OH and dried under vacuum. An elemental analysis showed no nitrogen. Anal. Found: %C, 36.64; %H, 0.29; %N, 0.85, %Cl 0.0; %F, 45.43; %O (by diff.), 16.79.

5. Tetrafluoroterephthalic Acid

A 3-l., 5-neck flask was fitted with a stirrer, gas inlet, gas outlet, thermometer, and addition funnel and cooled to -78°. Butyl lithium (48g. in 320g. of hexane solution, 0.74 moles) was placed in the flask and cooled to below -70°. Tetrahydrofuran (1 liter) was cooled to -70° and poured into the BuLi. The addition funnel was filled with p-$C_6F_4H_2$ (55.4g., 0.37 moles) in THF (75 ml) and this solution was slowly dropped into the reaction mixture so that the temperature never rose above -65°. The solution was stirred for 2 hours after the addition was completed. The mixture was then carbonated by bubbling CO_2 through at a rate such that the temperature did not . 'se above -65°. At the end of three hours the flow rate was 180 l/hr. The mixture was allowed to warm to room temperature with continued carbonation. After it reached room temperature the mixture was poured into 1200 ml of 6N HCl. The 2-phase mixture which developed was stripped of THF and about 600 ml of water before a solid began dropping out. As the residue became thicker the distillation was stopped. The mixture was cooled in ice water and filtered. The filter cake was dissolved in hot water and decolorized with activated charcoal. This solution was filtered and cooled to 0°. The white solid which formed was filtered off and dried over P_2O_5 to give 72g. (81% conversion) of tetrafluoroterephthalic acid, mp= 280-1°.

6. Monosilver Tetrafluoroterephthalate

A solution of tetrafluoroterephthalic acid (10.0g., 0.042 moles) in water (250ml) was heated to 50-60° with stirring. Silver oxide (4.87g., 0.021 moles) was added in small amounts as it appeared to react. The mixture was maintained at this temperature overnight, and a white precipitate formed. The mixture was heated to 100° and enough water was added to dissolve the silver salt. The mixture was then filtered and the filtrate was concentrated to about 1/3 its original volume. It was cooled in ice water and the white solid which formed was filtered off. The filtrate was again concentrated, cooled in ice water, and filtered. The two filter cakes were combined dried over P_2O_5 and found to weigh 11g. This represents a 76% yield of the monosilver salt. Anal. Calcd. for $C_8HF_4O_4Ag$: %Ag, 31. Found: %Ag, 39.

7. Tetrafluoroterephthalyl Mononitrite

Monosilver tetrafluoroterephthalate (5.0g., 14.5 mmoles) was placed in a small flask fitted with a gas inlet and stirrer. The flask was evacuated and frozen in liquid air and ClNO (2.6g., 40 mmoles) was condensed in.

The flask was allowed to warm and as the pressure built to atmospheric, the excess ClNO was removed. After all the ClNO has vaporized the flask was evacuated and heated to 250°. A small amount of yellow crystals sublimed into the gas outlet tube. These crystals have not yet been analyzed. However, it appears that the reaction with ClNO was not complete.

8. 1, 4-Diaminotetrafluorobenzene

1, 4-Dihydrazinotetrafluorobenzene-bis-acetophenone hydrazone (45.0g., 10.8 mmoles) was reacted with zinc (141g., 2.16 moles) in acetic acid (860 ml) at reflux temperature for 3 1/2 hours. The mixture was then filtered, washed with water (1250 ml) and extracted with ether in a Soxhlet. The ether extract was labelled Sol. A. The water washings were combined with the original filtrate and extracted with benzene (five 375-ml portions). This benzene extract was then washed with H_2O (five 250-ml portions). After separation from H_2O the benzene extract was labelled Sol. B. The aqueous washings from Sol. B were neutralized with NaOH and extracted with ethyl ether. This ether extract was labelled Sol. C. Solutions A, B, and C were combined, dried over $MgSO_4$, filtered and stripped of solvent. The dark red-brown residue was sublimed under vacuum at 120-130° to give 2.3g. of a light tan solid. A melting point determination (95-120°) showed that the product was still impure.

C. Synthesis of Intermediates and Other Monomers

1. Attempted Synthesis of SF_5COOH

Vinylsulfur pentafluoride (1.35g., 8.7 mmoles) was placed in a 3-neck, 100-ml flask fitted with a stirrer, reflux condenser, and addition funnel containing a solution of $KMnO_4$ (2.5g., 16 mmoles) in acetone (27 ml) and H_2O (12 ml). The $KMnO_4$ solution was slowly dropped into the reaction pot and MnO_2 formed almost immediately. After stirring for several hours the MnO_2 was filtered off, and the filtrate was acidified with H_2SO_4. A white solid formed immediately. This solid was filtered off and an infrared spectrum was made, but it did not show the presence of an S-F group. The filtrate was extracted with ethyl ether and an infrared spectrum made of the extracts, but it did not show S-F absorption.

2. Chlorodifluoroacetyl Bromide

Into a 250-ml flask fitted with a thermometer, stirrer of reflux condenser were placed $CF_2ClCOOH$ (26.3g., 0.20 moles). The reaction vessel was heated to about 70° for 20 minutes and 100° for 4 hours. The product was then distilled on a spinning band column to produce 16.4g. (50% yield) of $CF_2ClCOBr$ boiling at 47-47.5°.

3. Difluoroketene

A 250-ml flask was fitted with a stirrer, reflux condenser vented to a -78° trap, and an addition funnel containing $CF_2ClCOBr$ (16.4g., 0.1 mole) dissolved in 50 ml of tetrahydrofuran. Into the flask were placed powdered Zn (40g., 0.66 mole), $ZnCl_2$ (trace) and tetrahydrofuran (100 ml). The contents of the flask were refluxed while the material from the addition funnel was slowly added. No product was caught in the cold trap and no $CF_2ClCOBr$ was recovered.

4. Attempted Synthesis of $CF_3OCF(NO)CF_2Cl$

A 1-1 Vycor flask was charged with $CF_3OCF{=}CF_2$ (1.63g., 9.86 mmoles) and ClNO (0.64g., 9.86 mmoles) and placed in sunlight for three days. There was no color change in the vapor. The product mixture was separated by GLC, and infrared spectra were made of the fractions obtained. The major products aside from starting material were NO_2 and N_2O. There was no evidence for the formation of a nitroso compound.

D. Polymerization

1. Thiocarbonyl Fluoride and Trifluoronitrosomethane

A 20-ml ampoule was charged with CF_3NO (0.495g., 5.0 mmoles) $CF_2{=}S$ (0.41g., 5.0 mmoles), $(C_2H_5)_3B$ (0.07g., 0.75 mmoles), O_2 (0.004g., 0.25 mmoles), and CF_2Cl_2 (8.29g.). The ampoule was placed in a -10° bath. After 15 days there was no change and the tube was allowed to warm to room temperature. There was still no change over the next 10 days. After 14 days at room temperature a yellow gum was observed in the bottom of the ampoule, but the solution and overgas remained blue. There was no further change after another 20 days. It appears that the CF_2S homopolymerized.

2. Thiocarbonyl Fluoride and Tetrafluoroethylene

A 20-ml. ampoule was charged with $CF_2{=}CF_2$ (0.50g., 5.0 mmoles), $CF_2{=}S$ (0.41g., 5.0 mmoles), $(C_2H_5)_3B$ (0.07g., 0.75 mmoles), O_2 (0.004g., 0.25 mmoles), and CF_2Cl_2 (7.83g.). The ampoule was placed in a -10° bath, the following day it contained a white solid. The overgas was removed to a separate ampoule and an infrared spectrum was made. The only material it showed to be present was CF_2Cl_2 and $CF_2{=}CF_2$. The material which was left after the volatiles were removed was a white gum. An infrared spectrum showed absorption at 9.1-9.2 and 9.65 microns.

3. Thiocarbonyl Fluoride, Trifluoronitrosomethane and Tetrafluoroethylene

A 20-ml ampoule was charged with CF_3NO (0.50g., 5.0 mmoles) $CF_2{=}CF_2$ (0.50g., 5.0 mmoles), $CF_2{=}S$ (0.41g., 5.0 moles), $(C_2H_5)_3B$ (0.13g., 1.1 mmoles), O_2 (0.006g., 0.4 mmoles) and CF_2Cl_2 (7.54g.). The ampoule was placed in a -10° bath. After 15 days there was no change, and it was allowed to warm to room temperature. After 4 days the ampoule contained a brown gum and the overgas and solution had lost their blue color. The volatiles were removed to a separate ampoule leaving a brown gum. Analysis of this material is not complete. The volatiles were separated by GLC and infrared spectra showed them to contain both C_2F_4 and CF_2S but no CF_3NO.

4. Tetrafluoroethylene and Trifluoronitrosomethane

Two solutions, A and B, were made. Solution A contained 0.214 g. of Ph_4Sn per 150ml of cyclohexane. Solution B contained 1 mole of $AlBr_3$ and 2.5 mmole of VCl_4 per liter of cyclohexane.

A 20-ml ampoule was charged with CF_3NO (0.43g., 4.3 moles) $CF_2{=}CF_2$ (0.43 g., 4.3 mmoles), Sol. A (15 ml), Sol. B (0.1 ml), and cyclohexane (5 ml) and placed in a 10° bath. After 24 hours most of the blue color had disappeared and a very viscous liquid was present. After standing for a week at 10° and 2 weeks at room temperature there was no apparent change.

5. Tetrafluoroethylene, Trifluoronitrosomethane and $CF_3SCF(NO)CF_2Cl$

A 45-ml ampoule was charged with $CF_3SCF(NO)CF_2Cl$ (0.18g., 0.73 mmoles), CF_3NO (0.289g., 2.92 mmoles) and C_2F_4 (0.365g., 3.65 mmoles) and placed in a -20° bath. By morning the ampoule contained a viscous blue liquid and a pale blue overgas. After several days the blue color disappeared. The volatiles were removed and a viscous liquid was left. An infrared spectrum of the volatiles showed them to contain all three reactants. An infrared spectrum of the viscous liquid product was identical to a spectrum of CF_3NO/CF_2=CF_2 copolymer.

6. Tetrafluoroethylene, Nitrosyl Chloride and Ethyl Mercaptan

An 80-ml glass tube was cooled in liquid N_2 and charged with C_2H_5SH (0.74g., 12 mmoles), ClNO (0.79g., 12 mmoles), and CF_2=CF_2 (1.2g., 12 mmoles). As soon as the C_2H_5SH and ClNO were both placed in the tube it turned a deep red color. It was transferred to a -30° bath and the color disappeared. The tube remained in the bath for 3 days. It was warmed to room temperature and an infrared spectrum of the overgas showed only starting material. When this overgas was frozen in liquid N_2 it again produced the deep red solid.

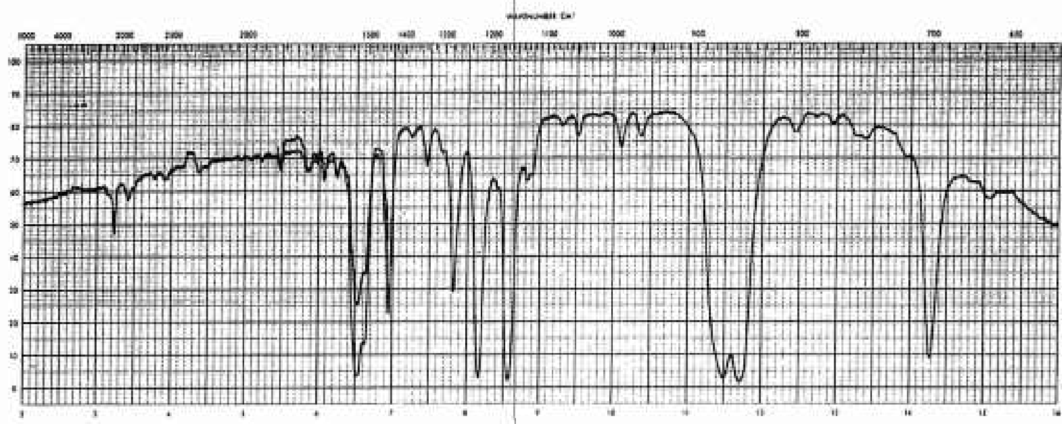


Figure 1. Infrared Spectrum of 1, 2, 4, 5-Tetrafluorobenzene

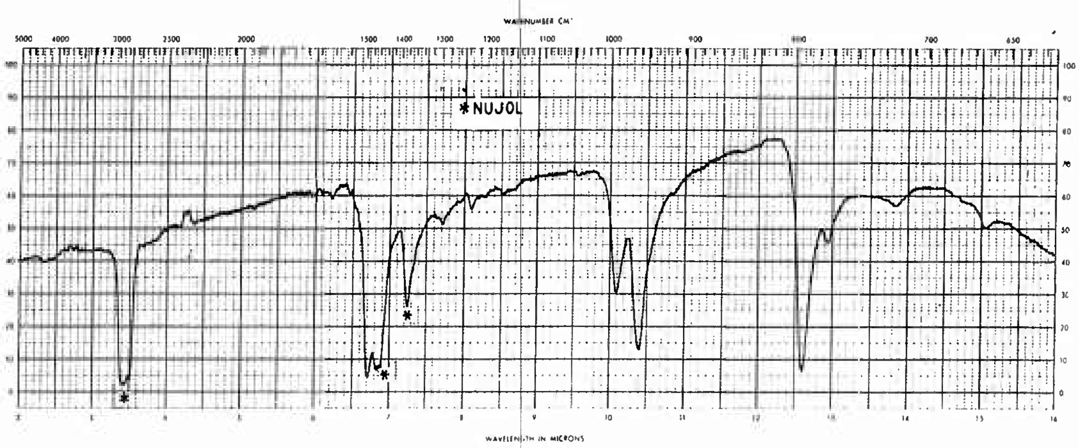


Figure 2. Infrared Spectrum of 1, 4-Dibromobenzene

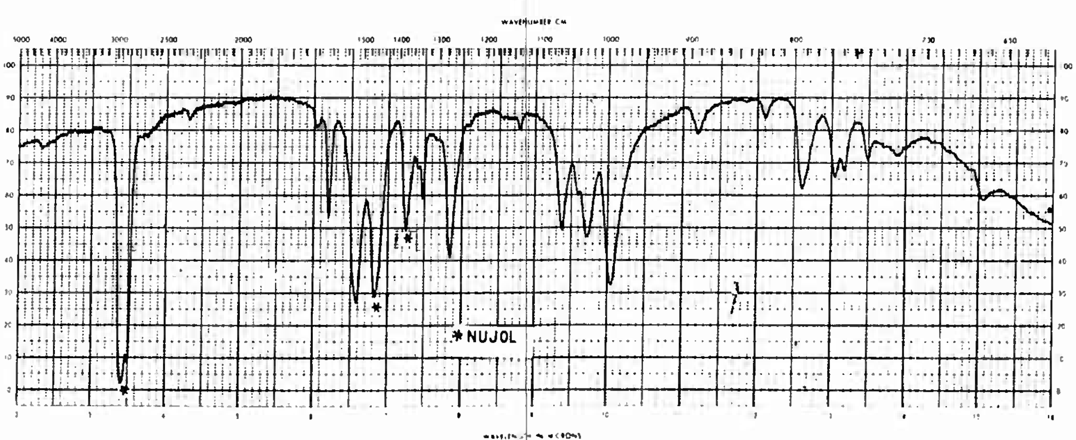


Figure 3. Infrared Spectrum of Unidentified Product From Reaction of Pentafluorophenyllithium and Nitrosyl Chloride

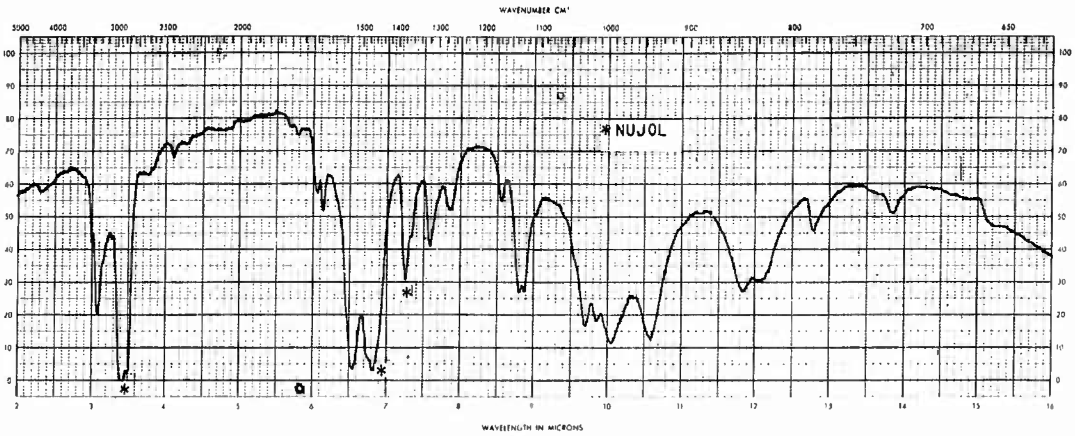


Figure 4. Infrared Spectrum of Pentafluorophenylhydrazine

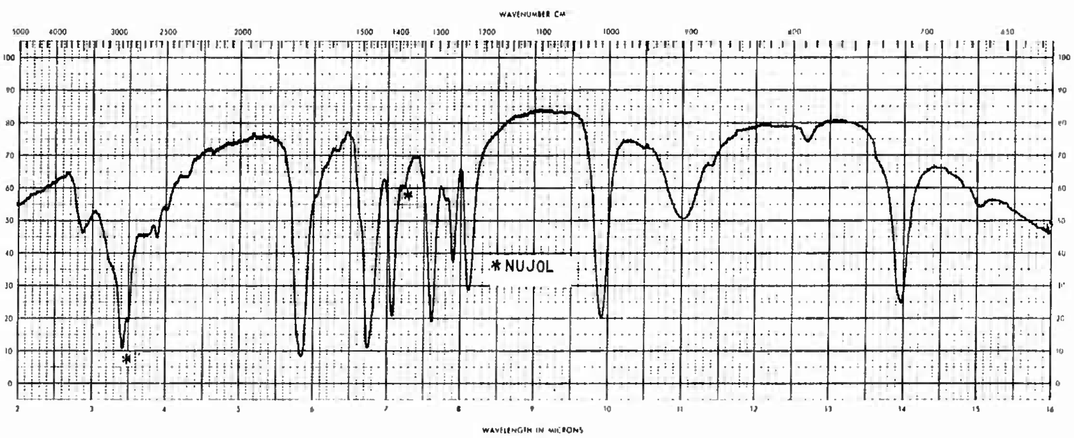


Figure 5. Infrared Spectrum of Tetrafluoroterephthalic Acid

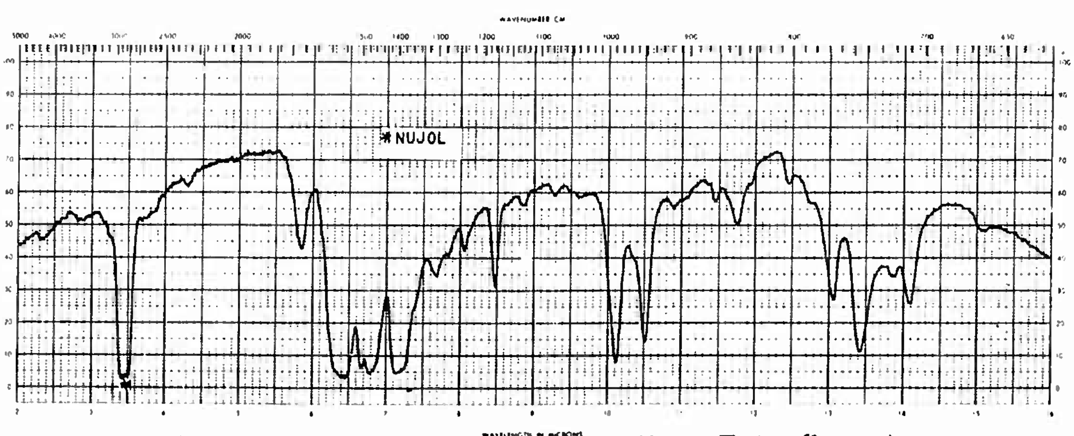


Figure 6. Infrared Spectrum of Monosilver Tetrafluoroterephthalate

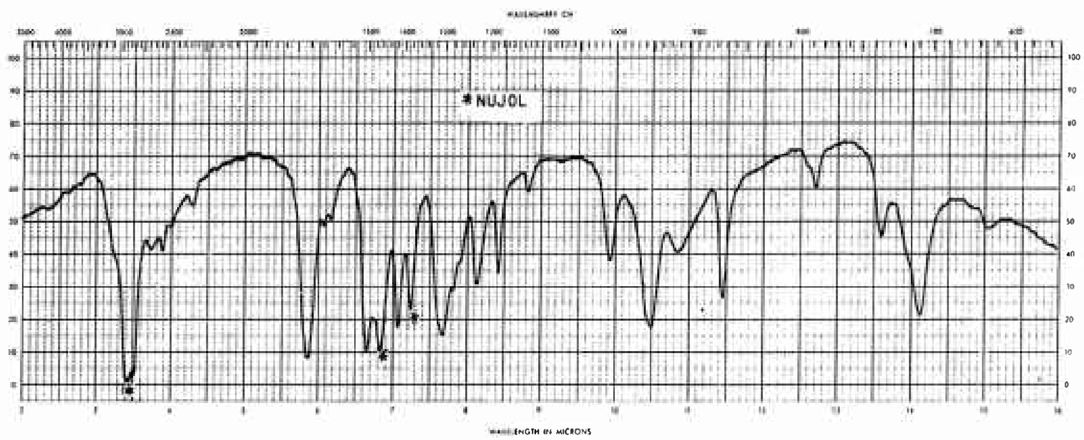


Figure 7. Infrared Spectrum of Tetrafluoroterephthalyl Mononitrite

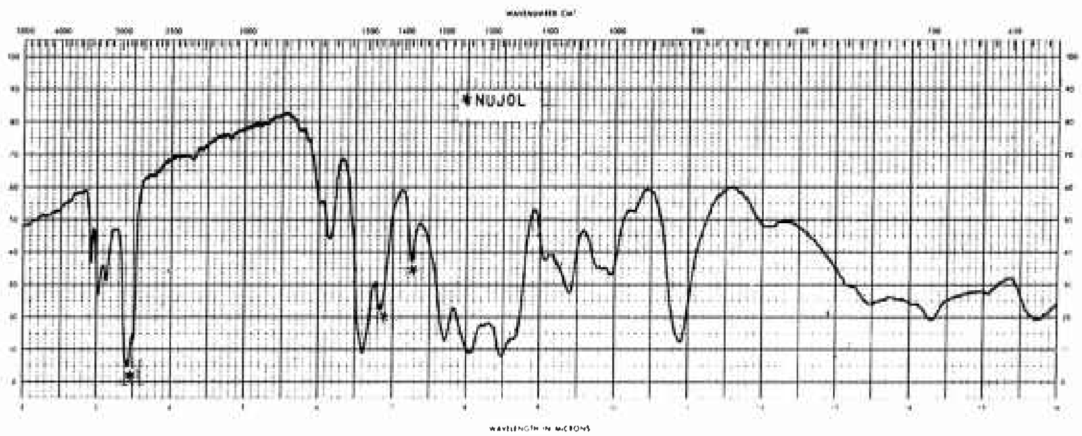


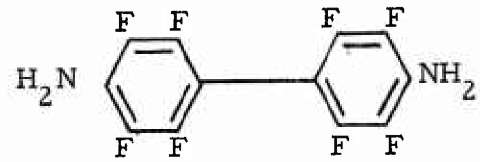
Figure 8. Infrared Spectrum of 1, 4-Diaminotetrafluoro-benzene

IV. MONOMER LIST

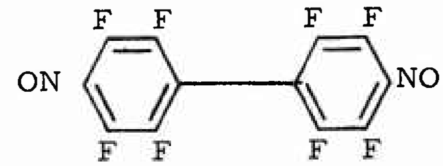
The monomers listed below have been assigned the identification numbers shown. These numbers will be used frequently throughout future reports in place of cumbersome nomenclature or structures. A complete list of monomer number assignments will be given in each report.

Number	Monomer
400	$F_2C{=}S$
401	C_6F_5NO
402	$SF_5CH{=}CH_2$
403	$CF_3SCF{=}CF_2$
404	$(CF_3)_2C{=}S$
405	$CF_3N{=}SF_2$
406	C_6H_5NO
407	$[CF_3CF_2CH_2CH_2Si(CH_3)O]_3$
408	$[CF_3CF_2CH_2CH_2Si(CH_3)O]_4$
409 (Tentative)	$CF_3SCF(NO)CF_2Cl$

410 (Tentative)



411 (Tentative)



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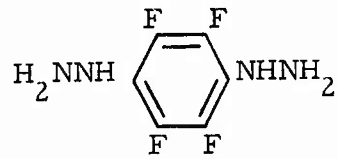

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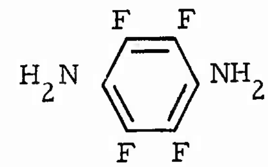

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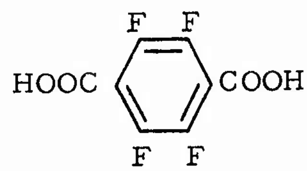

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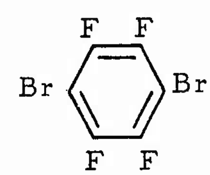

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SYNTHESIS AND POLYMERIZATION OF FLUORINATED SULFUR MODIFIED NITROSO RUBBER - Eugene C. Stump and Calvin D. Padgett Quarterly Report No. 4, 1 April 1964 through 30 June 1964. 22 pp., 8 Figures, Contract DA-19-129-(AMC)-152(N)-(OI 9116), Project No. 1K024401A113, Unclassified

Attempts to prepare $SF_5CF(NO)CF_2Cl$ and C_2H_5SNO are described. Several mono- and difunctional perfluoroaromatic monomers and precursors have been synthesized. Routes to SF_5COOH and SF_5CF_2COOH are discussed. Low temperature polymerization of $F_2C{=}S$ with CF_3NO, $CF_2{=}CF_2$ and $CF_3NO/CF_2{=}CF_2$ has been attempted using a triethylborane/oxygen catalyst. A coordination catalyst has been used to polymerize $CF_3NO/CF_2{=}CF_2$. The new monomer $CF_3SCF(NO)CF_2Cl$ is relatively non-reactive compared with CF_3NO.

UNCLASSIFIED

1. Nitroso compounds
2. Sulfur-fluorine compounds
3. Polymers
4. Fluoroaromatic compounds
5. Contract DA-19-129-(AMC)-152(N)(OI 9116)

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